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(54) Title: ANODES PRODUCED FROM METAL POWDERS (57) Abstract <p>A process for producing a sintered body, especially a consumable anode, from a metal powder, characterised in that during or prior to sintering of an agglomerated or compacted body of a metal powder, consisting of a single metal, a metal alloy or a mixture of two or more metals and/or alloys, an activating film is present on the surface of some or all of the powder particles, whereby sintering of the particles is activated, and during subsequent stages of the process the film is at least partially destroyed and removed. The activating film is formed by treating the powder with an activator such as sulphur, selenium, tellurium, or a halogen, or a compound thereof, which reacts with the metal to form the film.</p>		

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ANODES PRODUCED FROM METAL POWDERS

This invention relates to a process for preparing, from metal powders, anodes which are suitable for electrodeposition, particularly electroplating, electroforming, and other processes where consumable
5 metal anodes are employed.

In the art of electroplating, consumable metal or metal alloy anodes should ideally have good dissolution characteristics in the electrolyte bath and should not generate excessive amounts of sludge or insoluble
10 fines. Where multiple anodes are used in anode baskets or anode bags, the anodes should also be of a suitable shape and size such that they will pack well in the basket, will not fall through the mesh of the basket, nor be prone to bridging in the basket. In
15 addition, they should be easy to handle and not have sharp edges that will damage the anode basket or bag. Such anodes should also be strong enough to be transported without breakage or crumbling of the edges by auto-attrition.

20 Most anodes presently used in the industry are produced either by electrodeposition or by casting or granulation of molten material. There should, however,



be considerable economic and technical advantage to be gained if such anodes could be produced from powders. Thus shape and size could be accurately controlled and energy requirements for some form of agglomeration, or compaction, and sintering could be substantially less than that required for melting and casting, or for electrolytic forming of anodes.

U.S. Patent No. 3,943,048 discloses a powder metallurgical technique for making anodes with a density in excess of about 70 percent of theoretical density which contain dispersed additives which act as electrode activators and electroplating bath additives. To date, however, it has proved difficult to produce anodes by such methods that have suitable electrolytic characteristics, that do not produce excessive fines as a result of early erosion of the areas of contact or necks between particles and that are strong enough to withstand bulk transport without breakage or uneconomic attrition.

It is therefore an object of the present invention to provide an economical process for producing anodes by powder metallurgical techniques which do not have the above-mentioned problems associated with them.

Powder metallurgy techniques have been developed to allow higher density products with improved mechanical properties to be produced. One such technique is "activated sintering" (described in "Sintering and Related Phenomena", Proceedings of the International Conference held in June 1965 at the



University of Notre Dame, Gordon and Breach, Science Publishers p.807-827).

U.S. patent 2,942,334 describes a process for sulphur-activated sintering of iron powder which has been treated with hydrogen sulphide gas or to which has been added powdered metallic sulphides. Physical properties of sintered products were improved by the presence of sulphides which had a scavenging effect upon surface iron oxide and by the formation of a liquid phase therewith. Experiments conducted by Bockstiegel (Powder Metallurgy, 10, 171 (1962)) indicate that sulphur-activated sintering of iron powder and the retention of sulphur in pores may be an effective means of achieving pore closure to allow satisfactory case hardening. The reported results indicate that total porosity increased slightly with increased sulphur additions.

While it might be thought obvious to apply the above teachings to the production of anodes, there are a number of reasons why sulphur-activated sintering would not be expected to provide sintered anodes with improved characteristics. These include:

- (a) the products have a relatively low density;
- (b) the products are relatively high in sulphur;
- and
- (c) the products suffer from exacerbated swelling problems.

For anodes made by powder metallurgy techniques, electrochemical attack and erosion first occur at areas



of contact or "necks" between particles. As sulphur-activated sintering generally does not increase the compact density it would not be expected to decrease the amount of "necking" and hence, the rate of erosion and the amount of fines or sludge produced.

Sulphur-activated sintering results in a sintered product containing relatively high levels of sulphur. The method of U.S. Patent 2,942,334 results in a compact containing 0.275 to 0.375 percent by weight of sulphur. In the case of the Bockstiegel disclosure, residual sulphur is retained to effect pore closure. High residual sulphur levels are considered unacceptable for many anodes (see for example Chatterjee and Ray, "Behavior of Nickel Anodes in Plating Electrolytes" Electroplating and Finishing, August, 1967, 244-247).

In some cases the poor performance of anodes produced from metal powders, particularly those containing nickel, is due to an irreversible swelling that occurs during sintering (Australian Patent Application No. 53279/79). The swelling is apparently associated with the generation of large volumes of gases, recrystallization and reordering of the metal structure which cause individual powder particles to rupture. As a result, anodes during electrolysis are readily eroded to produce excessive fines or sludge. The swelling can be reduced if impurities such as sulphur and carbon present in powders (such as those produced by the Sheritt Gordon Process) are first eliminated by heating the powder in a nitrogen,



hydrogen or other suitable atmosphere at a temperature in the range 550-960°C.

As sulphur impurities can cause swelling, the use of sulphur-activated sintering to produce anodes could be expected to exacerbate the swelling problem.

There is prior art which suggests that a critical amount of sulphur may actually improve the electrolytic characteristics of nickel anodes by providing smooth corrosion and eliminating passivity (for example U.S. Patent No. 2,392,708 suggests a range of 0.007 to 0.11 percent while Canadian Patent No. 765,384 suggests a range of 0.01 to 0.025 percent). However, the inclusion of such levels of sulphur in sintered anodes containing nickel powder would hitherto have been expected to have caused unacceptable swelling problems.

Contrary to the above indications, it has now been found by the present inventors that improved anodes can be produced by powder metallurgical techniques involving activated sintering, especially sulphur-activated sintering. The anodes so produced have satisfactory dissolution properties in commonly used commercial electrolytes. They do not generate excessive or insoluble anode fines or sludges, and satisfactory erosion characteristics are achieved at relatively low compact densities which is also important from an energy point of view. The lower the compact density and the higher the metallic surface area the lower the current density and power requirement. In addition, although the anodes have a relatively low density, they are sufficiently strong



and ductile to enable them to withstand normal conditions encountered during handling and bulk transport.

5 The process of the present invention includes a step in which the content of sulphur (or other activator used) is reduced to a predetermined level in the final product; the performance of this step is actually assisted by the ability of the process to produce acceptable anodes with less than theoretical
10 density. Because the final sulphur level in the product can be thus controlled, it is possible to take advantage of the known benefits resulting from the presence of small amounts of sulphur. Furthermore, the present inventors have now shown that activated
15 sintering in accordance with this invention, can be used to overcome detrimental effects resulting from the use of raw materials which have not been pre-treated to minimize swelling problems.

20 It is generally accepted that the suitability of an anode made by a given method cannot be reliably predicted from the physical characteristics of the anode but must be determined by experiment. This is because most electrolytes are complex and interact in a complex manner with anodes according to mechanisms
25 which are not fully understood. Experiments have shown that the anodes produced by the method of the present invention have satisfactory dissolution properties in commonly used commercial electrolytes and can be used to produce high quality bright cathodes.

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It will be appreciated that the process of the invention may be used to form sintered bodies other than electroplating anodes.

5 A key feature of the process of the present invention is the presence during the initial stages of the sintering of an agglomerate or compact of a metal powder, of an activating film on the surface of some or all of the powder particles whereby sintering of the particles is activated. During subsequent stages of
10 the process the film is at least partially destroyed and removed.

According to the present invention, there is provided a process for producing a sintered body from a metal powder by sintering agglomerated or compacted
15 body of the powder, characterised in that:

- (i) prior to or during agglomeration or compaction, or sintering, the powder is treated with an activator which is capable of forming an activating film on the surface of
20 all or part of the powder particles and thereby giving rise to activation during the sintering step; and
- (ii) the sintered body is treated to reduce the amount of the activator therein to a
25 predetermined level.

The most preferred activators are those which react with the metal to form a sulphur-containing film,



which may consist of a sulphide of the metal, a metal-sulphur solid solution or a mixture of both. Thus, elemental sulphur or any suitable sulphur compound in gaseous liquid or solid form may be used.

5 Selenium or tellurium or their compounds may be similarly used. Members of Group VIIA of the Periodic Table, namely, the halogens (fluorine, chlorine, bromine and iodine) and their compounds, can likewise be used as activators. In this case, the activator, in
10 general, reacts with the metal to form a halide-containing film on the surface of some or all of the particles.

 The metal powder can consist of a single metal, a metal alloy, or a mixture of two or more metals and/or
15 alloys. Examples of such metal powders are nickel, copper, iron, cobalt, lead, zinc, cadmium, silver, gold, molybdenum, tungsten, titanium, aluminium chromium, platinum, palladium and tin, and mixtures or alloys of two or more of these metals. (These examples
20 are, of course, not intended to be limiting.)

 The main criterion is that the metal (or at least one metal component of a mixture or alloy) must be capable of forming a sulphide, selenide, telluride, or
25 halide film which can be partly or totally eliminated from the sintered body by an appropriate treatment, the preferred treatment being chemical reduction.

 In one preferred aspect, the present invention provides a method of producing sintered anodes from



metal powders, or mixtures of metal powders, or alloyed metal powders, comprising the steps of:-

- 5 (i) preparing a powder of suitable particle size distribution to give good agglomeration characteristics on balling, or good green strength on compaction;
- 10 (ii) sulphidizing the surface of all or of a portion of the particles of the metal powder or metal powder mixture prior to agglomeration or compaction; or blending a solid or liquid compound or mixture of compounds with the metal powders to be agglomerated or compacted in such a way that on subsequent heating of the agglomerated or compacted powders the added compounds will sulphidize the surface of some or all of the metallic particles in the compact or agglomerate;
- 15 (iii) agglomerating or compacting the powders, so treated or blended, by any standard hot or cold processes;
- 20 (iv) heating the compacted or agglomerated powder in an atmosphere and at a temperature that will allow sulphur- or sulphide-activated sintering to proceed;
- 25 (v) heating the sulphided agglomerates or compacts in an atmosphere and at a temperature that will remove at least part of



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the sulphidizing sulphur from the thus formed metal anode.

The process of the invention is particularly suitable for producing nickel and nickel alloy anodes.

- 5 The metallic powder particles can be produced by any commercial process such as precipitation from solution, atomization of molten metal, reduction of metal oxides, decomposition of metal-organics, or by the carbonyl process.
- 10 Preparation of the agglomerated or compacted mass of the powder may include:
- (a) treatment of the powder to remove impurities, and/or;
 - (b) reducing the particle size of the powder or
- 15 treatment modifying the particle size distribution, or to facilitate such reduction or modification.

- 20 Should the metal powders contain trace impurities that are likely to cause unacceptable swelling during sintering of the agglomerated or compacted powders, then the powders can be treated, prior to agglomeration or compaction, by a process substantially as described in Australian Patent Specification No. 53279/79 which, although specifically concerned with eliminating such
- 25 impurities from precipitated nickel powders, can also be used for the elimination of impurities from other metal powders.



The overall particle sizes of the powder for an anode will generally fall within the range 1-150 μ m and while not essential the powder should preferably have a fairly wide distribution of particle size within that range to allow pore filling to occur during agglomeration or compaction of the powder.

In this connection, it may be advantageous to reduce the particle size of a coarse powder or to change the particle size distribution of a powder by mixing a proportion of a powder of fine particle size with a powder of coarser particle size.

It is well known that it is difficult to reduce the particle size of high purity ductile metals, or to produce fine powder having particle sizes less than 45 μ m from coarser powders of such metals.

It has been found, however, that high purity metal powders can be rendered amenable to comminution if they contain, or have incorporated into them, suitable trace impurities such that on subsequent heat treatment of the powder, in a controlled atmosphere at an appropriate temperature, gases are generated within the particles and build up sufficient pressure to produce cracks and fissures in the particles.

The trace impurities can be any element or compound that, on subsequent heating of the powder in a suitable atmosphere, will generate sufficient gas pressure to fracture and fissure the particles. Accordingly, such impurities, for example, may be traces of a carbonate or a carboxylic acid that will



decompose on heating to thereby liberate carbon dioxide gas, or traces of a sulphate that will decompose liberating a sulphur oxide gas. Another example of an impurity is nitrogen, which may be present as a decomposable ammonium salt or as gas adsorbed, or occluded, in micro-cracks and pores of the powder and which, on heating of the powder, will expand to develop a sufficiently high gas pressure to cause swelling and cracking of the particles.

Alternatively, the impurity may be a trace of a substance that will react with the atmosphere in which the powder is heated to generate a gas pressure within the particles. Thus, sulphur in solid solution in the powder, or occluded traces of sulphides, sulphates, or oxides, will react with an atmosphere containing hydrogen gas producing, within the powder particles, hydrogen sulphide, sulphur oxides and/or water vapour. Other trace impurities, of course, may be used. The level of impurities necessary for satisfactory performance will vary considerably, depending on what kind of impurity is involved, and the optimum amount will therefore best be determined by experiment. As a guide, however, satisfactory results will generally be achieved at impurity levels of from 10 to 1000 ppm.

The atmosphere in which the powder is heated will depend on the nature of the trace impurities. If these are present as readily decomposable salts, or occluded gas, an inert or neutral atmosphere such as nitrogen, or carbon dioxide, or even static air, is suitable. On the other hand, if the trace impurities are, for example, sulphides, or sulphur in solid solution, it is



necessary to use a reactive atmosphere such as one containing hydrogen in order to produce the necessary gaseous products within the particles.

5 The temperature at which the powder containing the trace impurities is heated again depends on the nature of the impurities and the atmosphere in which the powder is heated. In general, the temperature must be high enough to generate the necessary gas pressure within the particles, but not so high as to allow
10 significant welding of the cracks, produced in the particles, to occur. Generally, a heat treatment period of ten minutes has been found adequate.

The particle size of the powder after comminution is influenced by the quantity of trace impurity
15 incorporated in the powder. For example, a nickel powder containing 110 ppm carbon and liberating, on heating in a nitrogen atmosphere, 12.8 cc of carbon dioxide per 100 g of powder reduced, on crushing, to a powder of finer average particle size than a similar
20 powder containing 40 ppm carbon and liberating 3.7 cc of carbon dioxide per 100 g of powder.

Once a metal powder of the appropriate form has been obtained, it can be agglomerated or compacted by any of the many techniques used in powder technology.
25 For example, it can be balled on a disc or in a drum, compacted hot or cold under pressure, or hot or cold rolled or extruded. Any of these methods and others known in the art can be used to form a compacted powder anode and the above examples are not intended to be
30 limiting. It is generally preferable, however, because



of the control over size, shape and density of an anode, to compact the powder in a die or mould under pressure. Reciprocating or roll presses can be used. The pressure required to form a green compact strong enough to handle depends on the nature of the metal powders being compacted, but will generally be in the range 150 to 1500 MPa and more usually in the range 500 to 800 MPa. Compaction temperature also depends on the nature of the metal powders being compacted, but generally cold compaction is found to be suitable. For large anodes isostatic pressing may be desirable.

As indicated above, the preferred activator is sulphur but one or more elements selected from the group of sulphur, selenium and tellurium (Group VIA of the Periodic Table) or fluorine, chlorine, bromine and iodine (Group VIIA of the Periodic Table) can also be used as the activator. The preferred embodiments discussed hereinafter will be particularly described with reference to the use of sulphur as the activator, but it will be understood that the methods and procedures described apply mutatis mutandis to the use of selenium and tellurium and the halogens also. Activation of the compacted mass by an activator such as sulphur may be accomplished by using a sulphidizing agent which can be any substance or substances that will cause a sulphur containing film such as a sulphide compound or a metal-sulphur solid solution to be formed on all or some of the metal particles in the anode, either prior to or during agglomeration or compaction, or during sintering of the anode. Obviously, if the purity of the anode is to be maintained it is undesirable for the sulphidizing agent to contain any



element, other than the metals comprising the anode, that cannot be removed from the anode either prior to or during sintering of the anode.

5 The sulphidizing agent can be a solid sulphide of one or more of the components of the anode or it can be solid or liquid sulphur, which is blended with the metal powders prior to agglomeration or compaction and which becomes effective when the agglomerated or compacted powder is heated. Alternatively, the surface
10 of all or of a portion of the powder particles that are to comprise the anode can be sulphidized with a gas, liquid or solution prior to agglomeration or compaction. Any of these methods of incorporating the sulphidizing agent can be used and these methods are
15 not intended to be limiting, but because gaseous sulphidization of the surface of all or part of the powder particles prior to compaction or agglomeration provides a convenient method of distributing the activated sintering agent more uniformly and
20 efficiently throughout the anode, this form of sulphidization is preferred.

A further economic advantage of this gaseous method of sulphidization is that, if necessary, it can be coupled with the aforementioned process described in
25 the Australian Patent Specification No. 53275/79, for removing from the powder trace impurities that cause swelling, during sintering, of compacts of the powder. Thus, the gaseous sulphidization of the powder can be achieved with little or no additional expenditure of
30 energy than is required for the pretreatment of the powder.



Gaseous sulphidization of metal powder particles can readily be achieved by heating the powder at a suitable temperature in an atmosphere containing an appropriate partial pressure of a sulphidizing (or sulphiding) vapour such as sulphur or hydrogen sulphide. The partial pressure of the sulphidizing gas (vapour) in the treatment atmosphere will depend on the metal being sulphidized and the temperature chosen for sulphidization. As will be readily understood by those skilled in the art, the partial pressure of sulphur (in each of its equilibrium gaseous polymeric forms) in the sulphidizing gas must be above the partial pressure of sulphur due to decomposition of solid sulphide or solid solution it is desired to form. On the other hand, the partial pressure of the sulphidizing vapour should not be so high that it exceeds the stability field of the particular sulphide or solid solution, or causes too rapid or too extensive conversion of metal to sulphide to occur.

The sulphidizing gas can be mixed directly with the diluent or carrier gas to give the desired partial pressure of sulphidizing vapour, or the carrier gas, for example, hydrogen or nitrogen can be passed over a material such as sulphur or a sulphide, for example pyrite (FeS_2), which can be heated to an appropriate temperature to generate the desired partial pressure of sulphidizing vapour in the carrier gas.

The temperature of sulphidization for pretreatment of the powder can be any convenient temperature, but it is desirable that it be below the temperature of



melting of any of the metals being treated or of any compound or solid solution formed by the treatment.

5 Gaseous sulphidization can be done in any standard furnace but preferably in one where the powder is kept moving during the reaction, such as a fluid bed furnace or rotary kiln.

10 The quantity of sulphidizing agent required to effectively activate sintering varies somewhat with the type of sulphide film formed and the manner of incorporating the sulphidizing agent. Sufficient sulphidizing agent must be present to activate sintering but it should not be so much as to cause excessive swelling or rupturing of the anode during removal of the added sulphur in the final sintering process. Consequently, the optimum amount of sulphidizing agent is best determined experimentally for the particular metal or metals comprising the anode and for the particular type of sulphidizing agent and its mode of incorporation. Preferably, the sulphur content of the green anode (i.e., prior to sintering) is in the range 0.1 to 2.0 per cent of the weight of the anode.

25 The sintering of the agglomerated or compacted powder containing the sulphidizing agent can be done in any readily available muffle or sintering furnace such as the continuous belt or the pusher type furnaces commonly used in the powder metallurgical industry.

The initial activated sintering temperature should be high enough to bring about activated neck growth or



diffusion between the metal powder particles comprising the anode. Thus the actual sintering temperature will depend on the metals being sintered and the nature of the sulphide film. If practicable, it is desirable that the activated sintering temperature be above the melting point of the sulphidizing agent or of the sulphide film formed, but below the temperature at which the film decomposes. For instance, if heazlewoodite (Ni_3S_2) is incorporated as the sulphidizing agent in a nickel powder compact, either as a powder or by presulphidizing the nickel metal powder, then it is desirable that the activated sintering temperature be above the Ni-S eutectic temperature (640°C) and preferably above the melting point of heazlewoodite ($\text{mp. } 790^\circ\text{C}$).

The time required to activate the sintering is quite short, particularly if the sulphidizing agent is incorporated by presulphidizing all or part of the powder particles. In many cases, sintering will be activated in the time required to heat the anodes to the temperature of the reduction process (the reducing sintering temperature"). When the activating agent is incorporated as a solid sulphide powder, for example powdered heazlewoodite (Ni_3S_2) or pyrrhotite (FeS), it may prove beneficial to hold the anodes at the activating sintering temperature for 10 to 30 minutes to allow time for the sulphide film to be distributed uniformly throughout the compact.

The activated sintering atmosphere is also influenced by the nature of the sulphidizing agent and the manner in which it is incorporated in the anode.



Generally, activation is so rapid that the final (usually reducing) sintering atmosphere can be used throughout the sintering operations. Occasionally, however, it can prove beneficial to activate the sintering in an inert atmosphere, such as nitrogen, to allow thorough and uniform sulphidizing of the particles to take place before reduction or decomposition of the sulphide film commences.

The final stage of the process involves the reduction of an amount of sulphur to a predetermined level which may be a level considered to provide optimum electrochemical characteristics. This operation generally requires a reducing atmosphere. Hydrogen gas, syn-gas (cracked ammonia) and other hydrogen containing atmospheres, commonly used to remove sulphur, have been found to be suitable, but any other atmosphere that can be used to eliminate all or part of the sulphur from a particular anode can be used.

The reducing sintering temperature must be high enough to decompose the sulphide film and remove the added sulphur while concomitantly maintaining rapid interdiffusion of the metal of the powder particles. Generally, the closer the sintering temperature approaches the melting point of the metal or metals comprising the anode the faster the rate of interdiffusion of the metals. On the other hand, the higher the temperature the greater the energy consumption for a given sintering period and the shorter the life of the sintering furnace and ancilliary equipment such as sinter belts. For nickel



and many nickel alloy anodes, final sintering temperatures between 800° and 1200°C can be used with temperatures near 1000°C providing a suitable compromise between rate of interdiffusion, and
5 excessive energy consumption and equipment constraints.

The amount of neck growth between particles, and so the strength and density of sintered anodes, increases with increase in sintering period. Consequently, the reducing sintering period should be
10 as long as economically practicable or such as is compatible with product requirements. Generally, we have found sintering periods of between one half and two hours, which are commonly used in the metallurgical
15 industry for sintering alloy briquettes or powder metallurgical parts, are adequate to remove the added sulphur and obtain strong bonding of the metal particles.

Example 1 demonstrates the above-described process for reducing the particle size or changing the particle
20 size distribution of a metal powder.

EXAMPLE 1

A precipitated high purity (99.8%) nickel powder containing trace impurities, including a carboxylic acid (total carbon analysis, 70 ppm), gave the
25 following screen analysis:



	Particle size (μm)	Percent
	+150	4.9
	-150 +100	24.8
	-100 + 75	53.0
5	- 75 + 45	16.7
	-45	0.6

After grinding 100 g of this powder for 4 minutes in a gyratory mill, less than 3 per cent of the powder had a particle size of less than 45 μm . However, when, according to the present disclosure, the powder was heated to 760°C for half an hour in a nitrogen atmosphere, then cooled, and 100 g of the preheated powder ground under the same conditions as above, more than 75 per cent of the powder had a particle size of less than 45 μm .

The following comparative examples demonstrate the use of the process of the present invention but should not be construed as limiting thereon. Examples 2, 4 and 6 show the results obtained in the absence of the application of the process of the present invention; Examples 3, 5 and 7 demonstrate, respectively, the improved results obtained when the nickel powders used in Examples 2, 4 and 6 are treated according to the present invention.

25 EXAMPLE 2

High purity (99.8%) precipitated nickel powder containing trace impurities including 70 ppm carbon and 220 ppm sulphur was pretreated in nitrogen at 750°C



according to the process described in our Australian Patent Specification NO. 53279/79. The treated nickel powder was mixed with "Atomet" iron powder, containing 150 ppm sulphur, in the ratio 70 Ni/30 Fe (w/w). The blended powders (sample weight 15 g) were cold compacted in a 25 mm die at 616 MPa for 3 seconds and the green compact sintered in a hydrogen atmosphere at 960°C for 1 hour. When this compact was used as an anode in a standard bright electroplating bath the anode residue (i.e.

wt. of fines in anode bag)
original anode wt.) was 3.5%

EXAMPLE 3

The high purity nickel powder used in Example 2 was pretreated by the process described in our Australian Patent Specification No. 53279/79 and was then treated, according to the present invention, in a sulphidizing atmosphere of hydrogen containing 1% hydrogen sulphide at 380°C in a fluidized bed reactor for a period of 1 hour. After this sulphidizing treatment the nickel powder contained 2850ppm sulphur and an x-ray powder diffractogram of the sulphidized nickel indicated the presence of Ni_3S_2 on the surface of the particles.

This sulphidized nickel powder was mixed with "Atomet" iron powder in the same proportions and compacted and sintered in the same manner as the compact in Example 2. After sintering, the sulphur content of the compact had been reduced to 130 ppm and an x-ray diffractogram of the sintered compact gave no



evidence of the presence of Ni_3S_2 or any other sulphur compound.

When this compact was used as an anode in a standard bright electroplating bath the anode residue was 1.1%.

EXAMPLE 4

High purity (99.8%) precipitated nickel powder, containing trace impurities including 70 ppm carbon and 220 ppm sulphur, was mixed with "Atomet" iron powder, containing 150 ppm sulphur, in the ratio 70 Ni/30 Fe w/w. The blended powders (sample wt:15 g) were cold compacted in a 25 mm die at 616 MPa for 3 seconds and the green compact sintered in a hydrogen atmosphere at 960°C for 1 hour. When this compact was used as an anode in a standard bright electroplating bath the anode residue was 4.4%.

EXAMPLE 5

The high purity nickel powder used in Example 4 was treated according to the present invention in a sulphidizing atmosphere of hydrogen containing 1% hydrogen sulphide at 380°C in a fluidized bed reactor for a period of 1 hour. After this sulphidizing treatment the nickel powder contained 3000 ppm sulphur and an x-ray powder diffractogram of the sulphidized nickel indicated the presence of Ni_3S_2 on the surface of the particles.



The sulphidized nickel powder was mixed with "Atomet" iron powder in the same proportions and compacted and sintered in the same manner as the compact in Example 4. After sintering, the sulphur content of the compact had been reduced to 100 ppm and an x-ray diffractogram of the sintered compact gave no evidence of the presence of Ni_3S_2 or any other sulphur compound.

When this compact was used as an anode in a standard bright electroplating bath the anode residue was 1.2%.

EXAMPLE 6

The nickel powder used in Example 2 was pretreated, as in Example 2, according to the process described in Australian Patent Specification No. 53279/79. This pretreated nickel powder was cold compacted in a 25 mm die at 616 Mpa for 3 seconds and the green compact sintered in a hydrogen atmosphere at 960°C for 1 hour. When this compact was used as an anode in a standard bright electroplating bath the anode residue was 3.4%.

EXAMPLE 7

The preheated nickel powder used in Example 6 was further treated, according to the present invention, in a sulphidizing atmosphere of nitrogen containing 20% hydrogen and 1% hydrogen sulphide at 380°C for 1 hour. After this sulphidizing treatment the nickel powder contained 2830 ppm sulphur and the X-ray powder



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diffraction diagram of the sulphidized nickel indicated the presence of Ni_3S_2 on the surface of the particles.

5 The sulphidized nickel powder was cold compacted and sintered in the same manner as the compact in Example 6. After sintering, the X-ray diffraction diagram of the compact gave no evidence of the presence of Ni_3S_2 or any other sulphur compound.

10 When this compact was used as an anode in the same bright electroplating bath as used for the compact in Example 6, the anode residue was 0.4%.



CLAIMS:

1. A process for producing a sintered body from a metal powder, characterised in that during at least the initial stages of the sintering of an agglomerate or compact of a metal powder, consisting of a single metal, a metal alloy or a mixture of two or more metals and/or alloys, an activating film is present on the surface of some or all of the powder particles, whereby sintering of the particles is activated, and during subsequent stages of the process the film is at least partially destroyed and removed.

2. A process for producing a sintered body from a metal powder, consisting of a single metal, a metal alloy or a mixture of two or more metals and/or alloys, by sintering agglomerated or compacted body of the powder, characterised in that:

- (i) prior to or during agglomeration or compaction, or sintering, the powder is treated with an activator to form an activating film on the surface of all or part of the powder particles and thereby give rise to activation during the sintering step; and
- (ii) the sintered body is treated to reduce the amount of the activating film to a predetermined level.



3. A process as claimed in Claim 1 or Claim 2, characterised in that the activator is a substance which reacts with the metal to form a sulphur-containing film, consisting of a sulphide of the metal, a metal-sulphur solid solution or a mixture of both.

4. A process as claimed in Claim 1 or Claim 2, characterised in that the activator is a substance which reacts with the metal to form a film containing at least one element selected from the group consisting of sulphur, selenium and tellurium, said film consisting of a compound of the metal and said element, or a solid solution of the metal and the element, or both.

5. A process as claimed in Claim 3 or Claim 4, characterised in that the activator is elemental sulphur, selenium and/or tellurium.

6. A process as claimed in Claim 1 or Claim 2, characterised in that the activator is a substance which reacts with the metal to form a film containing at least one element selected from the group consisting of fluorine, chlorine, bromine and iodine.

7. A process as claimed in any one of Claims 1 to 6, characterised in that the metal powder comprises at least one metal selected from the group consisting of nickel, copper, iron, cobalt, lead, zinc, cadmium, silver, gold, molybdenum, tungsten, titanium, aluminium, chromium, platinum, palladium and tin.



8. A method as claimed in any one of Claims 1 to 7, characterised in that the metal powder is subjected to gaseous sulphidization of the surface of all or part of the powder particles prior to agglomeration or compaction.

9. A process as claimed in any one of Claims 3 to 8, characterised in that the sintered body is subjected to chemical reduction to destroy and remove all or part of the activating film.

10. A process as claimed in any one of Claims 1 to 9, for producing nickel and nickel alloy anodes.

11. A process as claimed in any one of Claims 1 to 10, characterised in that it includes the step of treating the metal powder, prior to agglomeration or compaction to remove impurities.

12. A process as claimed in any one of Claims 1 to 11, characterised in that it includes the step of treating the metal to reduce the particle size of the powder and/or to modify the particle size distribution of the powder, or to facilitate such reduction or modification.

13. A process as claimed in Claim 12, characterised in that the metal powder contains, or has incorporated into it, at least one trace impurity such that on subsequent heat treatment of the powder, gases are generated within the particles and build up sufficient pressure to produce cracks and fissures in the



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particles, thereby to render the particles more amenable to comminution.



INTERNATIONAL SEARCH REPORT

International Application No PCT/AU 83/00072

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ³ According to International Patent Classification (IPC) or to both National Classification and IPC Int. Cl. ³ B22F 1/00, 1/02, 3/16, 3/24, C25D 17/12		
II. FIELDS SEARCHED Minimum Documentation Searched ⁴ Classification System Classification Symbols IPC B22F 1/00, 1/02 Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁴		
AU; IPC as above; Australian Classification 15.85		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category [*]	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X	US, A, 2942334 (BLUE) 28 June 1960 (28.06.60)	(1,3-5, 7,8)
X	US, A, 3943048 (FISHER et al) 9 March 1976 (09.03.76) (& DE, A, 2408830, & FR,A,2219242)	(1-8, 10-12)
X	US, A, 4132547 (BUZZELLI et al) 2 January 1979 (02.01.79) (& GB, A, 1603716, & DE, A, 2821661, & FR, A, 2392506, & JP, A, 53147934)	(1-5,7, 9-13)
X	GB, A, 1443511 (SHERRITT GORDON MINES) 21 July 1976 (21.07.76) (& DE, A, 2407030 & FR, A, 2219530, & JP, A, 49115010)	(1,2,4,6,7, 9-12)
X	GB, A, 1128188 (MALLORY METALLURGICAL PRODUCTS) 25 September 1968 (25.09.68)	(1,2,6,7, 10-12)
X,Y	JP, A, 53003904 (SUMITOMO METAL MINI K.K.) 14 January 1978 (14.01.78) (DERWENT ENGLISH LANGUAGE ABSTRACT M11, 15158A/08)	(1-13)
X,Y	JP, A, 54112736 (SUMITOMO METAL MINI K.K.) 3 September 1979 (03.09.79) (DERWENT ENGLISH LANGUAGE ABSTRACT M11, 74426B/41) and (CHEMICAL ABSTRACTS, Volume 91, No.26, 219407)	(1-13)
X,Y	JP, A, 5389810 (TOKYO SHIBAURA DENKI K.K.) 8 August 1978 (08.08.78) (JAPATIC English Language Abstract)	(1-7, 9-12)
* Special categories of cited documents: ¹⁵ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "Z" document member of the same patent family		
IV. CERTIFICATION Date of the Actual Completion of the International Search ¹ 20 July 1983 (20.07.83) International Searching Authority ¹ Australian Patent Office Date of Mailing of this International Search Report ¹ 03 AUGUST 1983 (03-08-83) Signature of Authorized Officer ²⁰ P.F. Gotham <i>P.F. Gotham</i>		